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# Growth and characterization of pulsed laser deposited lead germanate glass optical waveguides.

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Submitted to Optical materials

## Abstract

Lead germanate thin films have been grown on BK7 and silica substrates, using pulsed excimer laser deposition (PLD) at wavelengths of 193nm and 248nm, from a bulk lead germanate target under various partial pressures of oxygen. The films produced vary in colour from brown, through clear, to yellow, and a parametric study has been undertaken of the film properties as a function of the growth conditions. The measured losses of the lead germanate films grown on glass substrates varied from ~2.5 $dBcm^{-1}$ to 7 $dBcm^{-1}$ depending on the oxygen pressure used during growth.

# Introduction

Pulsed laser deposition (PLD) has been extensively researched within the past decade as a comparatively fast, easy, and flexible technique for growing thin films of a wide range of materials [1]. Amorphous, polycrystalline, and single crystal layers are routinely grown, depending on experimental parameters that include target composition, substrate temperature, target-substrate distance, and the presence of an ambient gas, often oxygen, at low partial pressures. Recent successes in crystalline growth by PLD have permitted the demonstration of efficient lasing action in 2-10 μm thick layers of gadolinium gallium garnet, GGG, grown on YAG [2,3], and also Ti:sapphire, grown on undoped sapphire [4]. The losses reported in [3], of 0.3-0.5dBcm$^{-1}$, are among the lowest currently known to us, and indicate the potential of PLD for improved future growth of thin film optical waveguide devices.

Glasses, however, have in our experience proved more difficult to grow using PLD. Several early attempts to grow both silicate and phosphate glasses resulted in films which were opaque, and under scanning microscopic examination, revealed their structure to be composed of ~few μm sized particles only: no smooth, continuous and transparent films could be grown. Additionally, the choice of ablating laser wavelength has a distinct role to play: phosphate glasses do not grow at all well in our experience using 248 nm (KrF laser), whereas 193 nm (ArF) produces very smooth, transparent films. In this paper, we discuss the growth of lead germanate glasses, which have important use as laser hosts, and under appropriate growth conditions, can show appreciable photosensitivity. We will report here only on the growth and characterisation of the films, leaving the results of induced index change behaviour for

publication elsewhere.

The target glass composition in mole% is $55GeO_2$ - 20PbO- 10BaO- 10ZnO - $5K_2O$, with some glasses having a partial substitution of $Al^{3-}$ for $Zn^{3-}$. The bulk glasses were prepared from anhydrous oxide powders for Ge, Al, Zn, Pb, and anhydrous carbonate powders for Ba, and K. All chemicals were of analytical grade except for $GeO_2$, which was of electronic grade (99.999% purity, Aldrich Chemicals). Glass batches of 150-200g of powder were mixed for at least half an hour, in a clean glass container. Batches were melted in a platinum crucible, in an electrically heated furnace, in air, at temperatures between 1000° C, and 1250° C, depending on the glass. The melts were kept well stirred with a silica rod to achieve homogeneous mixing, and later refined to remove bubbles. The refined glass-melts were removed from the furnace at 1150° C, and cast into a prewarmed stainless steel mould, before being annealed in a muffle furnace at ~500° C.

The refractive index of these glasses is high, ($n_D$ = 1.812 ± 0.005), thus making them good candidates for use in nonlinear optical applications. Additionally, $GeO_2$ based glasses have better infrared transmission properties when compared to their $SiO_2$ based counterparts, with transmission extending up to 5.5μm in some materials [5]. This improved transmission is due to the intrinsic mass difference between germanium and silicon atoms, which in turn leads to smaller stable glass formation ranges in $GeO_2$ based glasses, compared to $SiO_2$ glasses [6]. The manufacture of multi-component germanate glasses without devitrification is therefore harder to achieve than in silica based systems, and requires more rapid quenching rates. This may be the reason for our successful growth via PLD, which now provides an easy route to rapid growth

of active waveguide devices. The lead germanate glass composition has a maximum phonon energy of 810 $cm^{-1}$. Efficient 1.9μm lasing action can therefore be achieved when $Tm^{3+}$ doping is used [7]. An active length of only 3 cm is required, and hence planar integrated optical devices are particularly attractive here, for applications in LIDAR and medicine.

## Deposition parameters.

Films were grown by PLD using bulk undoped, and 1wt% Nd:doped lead germanate glass targets, in an oxygen gas ambient atmosphere. The growth was performed using a typical PLD system, which includes a vacuum chamber capable of maintaining a base pressure of ~$10^{-6}$ mbar, and an LPX200 excimer laser operating at either 248 nm (KrF), or 193 nm (ArF). Oxygen was admitted into the chamber, once the working pressure of ~$10^{-5}$ mbar had been reached. The range of oxygen pressures investigated was from 5.0 x $10^{-3}$ mbar to 1.0 x $10^{-1}$ mbar. All other deposition parameters of interest are listed in table 1.

Both target and substrate were asynchronously rotated, in order to achieve a degree of radial uniformity. At the 8cm target-substrate distance used, the films produced showed pronounced interference ring patterns, indicating that film thickness peaked at the centre of the substrate. Film thicknesses were measured using profilometers (Tallystep, Alphastep), across a step region introduced at the edge of each film. Although the deposition times, and all other conditions were nominally identical for each growth run (apart from varying oxygen pressures for example), the resultant film thicknesses obtained varied between 1.8μm and 2.7μm. For equal deposition times, thicker films were produced at lower ambient oxygen pressures.

The substrates used were cleaned microscope slides and fused silica discs. The larger microscope slides (76 mm x 25 mm) enabled a study of the optical properties as a function of radial distance to be carried out. PLD typically produces films with stoichiometry that varies by only a small degree over ~ mm dimensions, but over larger ~cm distances variations in absorption, quality, or in the case of the films here, defect concentration, can be readily observed. At critical values of oxygen pressure, films were grown that showed the brown-clear-yellow colour trend on a single substrate. Although substrates may be held at elevated temperatures for crystalline film growth, room temperature deposition only was used here. For multicomponent targets, such as these glasses, stoichiometry variations between target and film can be exacerbated by deposition at elevated temperatures.

## Results and discussion.

The films obtained show distinct colour variations, depending on the ambient oxygen pressure used during growth. For low oxygen pressures, (~$10^{-3}$ mbar), the films were brown in colour. At higher pressures, (~$10^{-2}$ mbar), uncoloured films were produced, while for the highest pressures, (~$10^{-1}$ mbar), pale yellow to deeper yellow films were grown. All films showed good adhesion to the substrates, apart from those grown at the very highest oxygen pressure, which were opaque and flakey in character. Figure 1(a) shows transmission spectra of a set of films grown using 248 nm excimer laser deposition, within the oxygen pressure range of 1.5 x $10^{-2}$ mbar to 4 x $10^{-2}$ mbar. These films varied in colour from clear, to pale yellow. The short wavelength absorption edge is seen to shift progressively to higher wavelengths as the oxygen pressure increases. Figure 1(b) shows the value of absorption coefficient, at a wavelength of 400 nm, as a function of

oxygen pressure. This value of wavelength was chosen as it falls conveniently between the absorption edge, and region of high transparency. The data points in figure 1(b) have been obtained by normalising to the calculated film thickness, at film centre. The thicknesses were in turn evaluated from fringes seen in transmission, and the known refractive index.

Figure 2(a) and 2(b) show similar results for the 193 nm excimer laser grown films. While the trend is similar, the transmission losses of the 193 nm grown films are systematically lower than those grown using 248 nm excimer deposition.

The films show a high degree of photosensitivity, when illuminated by either c.w. (244 nm, 325 nm) or pulsed laser light (193 nm, 248 nm). These characteristics, and the induced $\Delta n$, and hence grating diffraction efficiency achievable, are the subject of a separate paper, and hence will not be addressed here.

There is a systematic difference in material surface appearance, as evidenced through atomic force microscopy (AFM) surface topographic scans, which depends on the excimer laser wavelength used for the PLD growth. This has been observed to a much more marked degree before, during our earlier experiments on the growth of phosphate glass films. Using 248 nm excimer deposition, only films which were composed of macroscopic particles (few μm to tens of μm) could be grown. The films were opaque due to the high level of scattering, and waveguide modes could not be observed. Using 193 nm excimer laser deposition produced transparent smooth films, with drastically improved optical properties.

Figures 3(a) and 3(b) show AFM scans for 5 μm x 5μm areas of films grown using 193 nm and 248 nm excimer laser deposition respectively. It is clear that while figure 3(a) shows a fairly uniform, continuous surface, with only a few isolated particulates, figure 3(b) shows a surface composed almost entirely of an assembly of particles. A count of particulates was performed for the films grown using 193 nm excimer deposition only. An area of 100μm by 100μm was scanned, using image thresholding and commercial image processing software, to build up a histogram of particulate size distribution. The results, shown in figure 4, reveal that the mean size lies between 0.2 and 0.4 μm, with very few particles greater than 1μm present. Clearly the presence of this sub-micron sized debris is undesirable.

Waveguide loss measurements were performed on the films produced. All guides were multimode as the index difference between film and substrate is large (~0.3), and the guides are ~2 μm thick. Losses were measured by both the sliding prism [8] and imaged streak technique [9]. Using the first method, a rutile right-angle prism was used to couple He-Ne laser light in to the waveguide, while a second identical prism coupled the light out. Measurements of the outcoupled power were made at various distances along the waveguide, as shown in figure 5. Figure 6 shows the final loss results for 5 such films, grown using 193 nm excimer laser deposition, under different pressures of oxygen. The losses vary between 4 dB $cm^{-1}$ and 7 dB $cm^{-1}$. Annealing has been carried out on samples of the films, but this has the adverse affect of reducing, or even eliminating, the photosensitivity that is also a goal of this work.

Films were also grown from ~1wt% Nd doped glass, using 248 nm excimer laser deposition. For these films, the substrate rotation axis was offset by ~ 1.5 cm in the lateral direction, with respect

to the target rotation axis, as shown in figure 7, thereby producing films with a more uniform central region. The losses for these films should therefore be reduced with respect to non-uniform films. Losses were measured between 2.1dB $cm^{-1}$ and 3.4 dB $cm^{-1}$, using the two prism technique. The fluorescence properties of the doped films were investigated by exciting from the side, using ~300 mW of 488 nm Ar ion laser light, and collecting fluorescent output from the top. Spectra were obtained at a wavelength centred around 900 nm, rather than the more usual ~1μm, due to the limitations imposed by the available detection equipment.

A typical film fluorescence spectrum is shown in figure 8. For comparison, a spectrum obtained from the bulk glass target material is also shown, and the two spectra have been normalised to the same peak height. The spectra were recorded using an Acton Research Corporation SpectraPro-275 triple grating spectrometer, fitted with a cryogenically cooled CCD array. No attempt has been made here to correct the spectra for instrument response, so the data presented is for qualitative comparison only. The difference in spectral profiles indicates a variation in the local environment for the Nd ion between film and bulk glass samples. Given the earlier results on colour, composition and surface topography differences between the bulk glass and the thin films obtained, the exact spectroscopic characteristics are also expected to a sensitive function of film stoichiometry.

The observable differences in colour between the films are a result of several factors. Quantitative energy dispersive x-ray analysis (EDX) measurements have been performed using a JEOL JSM-6400 scanning electron microscope with a PGT IMIX EDS system, on two samples grown at the extrema of the oxygen pressure range investigated. Interpretation of the results is

complicated by the variation between the thickness of the two films examined, and also the presence of the substrate (borosilicate glass), which also contains oxygen. There is a systematic difference between the percentage of oxygen in the films. Care needs to be exercised however, as the accuracy for light element analysis is notoriously poor using EDX. Using data that has been corrected for the oxygen background signal from the substrate, we find that there is almost 50% more oxygen in the film grown at a partial pressure of $3.5 \times 10^{-2}$ mbar, than one grown at $1 \times 10^{-2}$ mbar. By comparison, the EDX data for germanium and lead contents show only a difference of $\leq$ 10% between the two films for these elements.

Competition clearly exists between the germanium and lead atoms, for the available oxygen incorporated within the growing film. Although the comparison may be qualitative only, lead and germanium oxides, present as powder samples, show similar colour variation as a function of their oxidation state. Lead for example can be black ($Pb_2O$), orange-yellow ($Pb_2O_3$), or yellow (PbO). Germanium oxide powders may be black (GeO) or white ($GeO_2$). At this stage, however, it is not possible to further define the exact role of the material stoichiometry, without extended spectroscopic and material analysis.

## Conclusions

In summary, it is clear that film colour, waveguide losses, and surface topography are a function of the excimer laser wavelength used in PLD growth of these glass films. Under conditions of improved film thickness uniformity, films with losses as low as 2.1 dB $cm^{-1}$ were obtained. There is a sensitive balance between the inherent film transmission, the associated waveguide losses,

and the resultant photosensitivity, which needs to be taken account of in designing practical doped glass waveguide devices grown by this technique.

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## Figure Captions.

Figure 1(a). Spectrophotometer traces of PLD films grown using 248 nm excimer laser deposition. The oscillatory behaviour is due to interference within the thin glass layer.

Figure 1(b). Absorption coefficient, at a wavelength of 400 nm, derived from the traces in figure 1(a), plotted versus oxygen partial pressure used during film growth. The data has been corrected for the film thickness, deduced via interference fringe analysis.

Figure 2(a). Spectrophotometer traces of PLD films grown using 193 nm excimer laser deposition.

Figure 2(a). Absorption coefficient at a wavelength of 400 nm, derived from the traces in figure 2(a), plotted versus oxygen partial pressure used during film growth. A similar correction procedure has been performed for deduced film thickness.

Figure 3(a). AFM scan of the film surface for a 193 nm excimer laser PLD grown film. Note the apparent smooth surface, with micron sized individual particulates present.

Figure 3(b). AFM scan of the film surface for a 248 nm excimer laser PLD frown film. The scan here shows that the surface is composed of densely packed sub-micron sized glass particles.

Figure 4. Histogram of particulate sizes for typical film grown using 193 nm excimer laser deposition. The mean particulate size lies between 0.2 μm and 0.4 μm. The area scanned was 100 μm x 100μm.

Figure 5. Waveguide loss measurement results obtained using the imaged streak technique.The fit is a least squares best fit curve. Inferred losses for this film, which was grown at an oxygen partial pressure of $3.5 \times 10^{-2}$ mbar, are 4.5 dB $cm^{-1}$

Figure 6. Waveguide loss results for films grown using 193 excimer laser deposition, as a function of the oxygen partial pressure during growth. Higher pressure leads to lower losses within the pressure region investigated.

Figure 7. Off axis deposition arrangement used to achieve uniform thickness in the central film region.

Figure 8. Fluorescence spectra for an Nd:doped thin film (dashed line) and bulk glass target (solid line) in the wavelength region centred around 900 nm.

## Acknowledgements

We would like to acknowledge the Engineering and Physical Sciences Research Council (EPSRC) for research funding under grant no. GR/L28722. Stephen Barrington also acknowledges the receipt of an EPSRC studentship. We are also grateful to the Barbara Cressey of the Geology Department, and Ping Hua from the ORC for assistance with EDX analysis. Bill Brocklesby is also thanked for AFM assistance, Charlie Haythornthwaite for fluorescence measurements and Eleanor Tarbox for insightful discussions on glass properties.

| Parameter | KrF depositions | ArF depositions |
|---|---|---|
| Laser pulse energy | 160 mJ | 190 mJ |
| Spot size on target | 2.5mm x 8.5 mm | 2 mm x 6 mm |
| Laser energy density | 0.75 J $cm^{-2}$ | 1.6 J $cm^{-2}$ |
| Target-substrate distance | 8 cm | 8 cm |
| Pulse repetition rate | 20Hz | 8 Hz |
| Substrate temperature | Room temperature | Room temperature |
| Background pressure | 3.5 x $10^{-5}$ mbar | 3.5 x $10^{-5}$ mbar |
| Oxygen ambient pressure | 5.0 x $10^{-3}$ - 1.0 x $10^{-1}$ mbar | 1.5 x $10^{-2}$ - 5.0 x $10^{-2}$ mbar |
| Oxygen flow rate | Not recorded | 0.6 - 3.1 sccm |
| Number of pulses | 24000 | 21600- 63000 |
| Film thickness produced | 1.8 μm - 2.7 μm. | 1.2μm - 12 μm. |

Table 1.

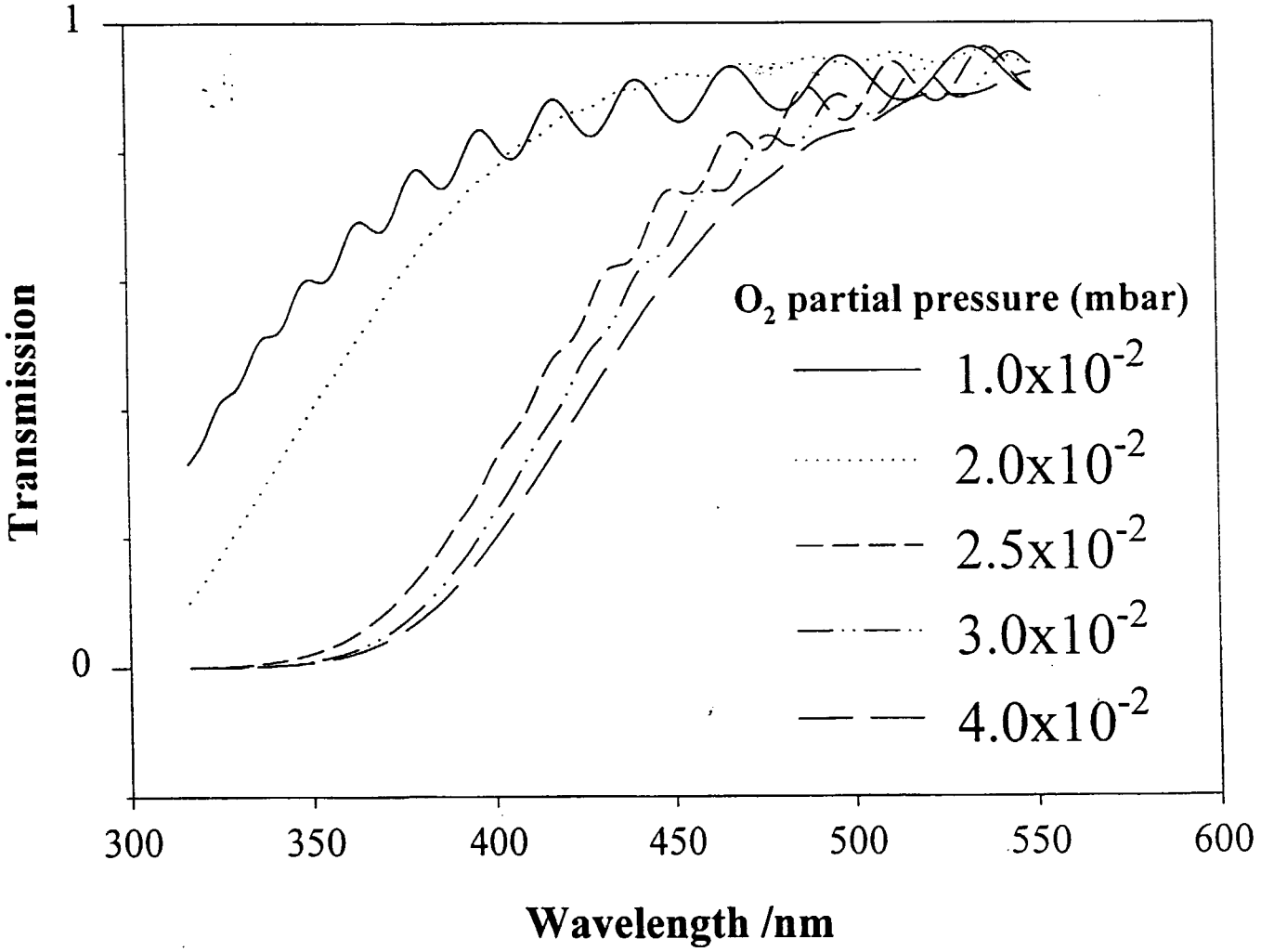
1
0
Transmission
300
350
400
450
500
550
600
Wavelength /nm
O2 partial pressure (mbar)
1.0x10-2
2.0x10-2
2.5x10-2
3.0x10-2
4.0x10-2

Fig 1(a)

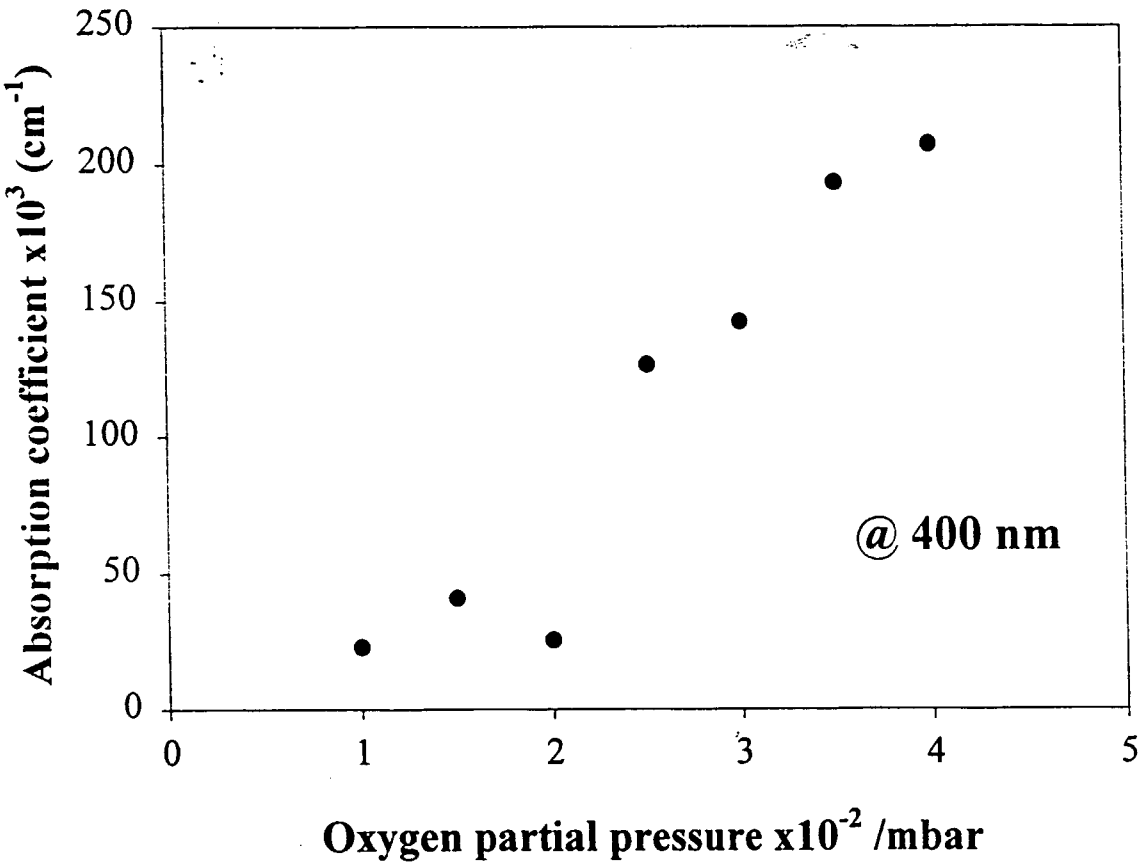
Absorption coefficient x10^3 (cm^-1)
250
200
150
100
50
0
0
1
2
3
4
5
@ 400 nm
Oxygen partial pressure x10^-2 /mbar

Fig 1(b)

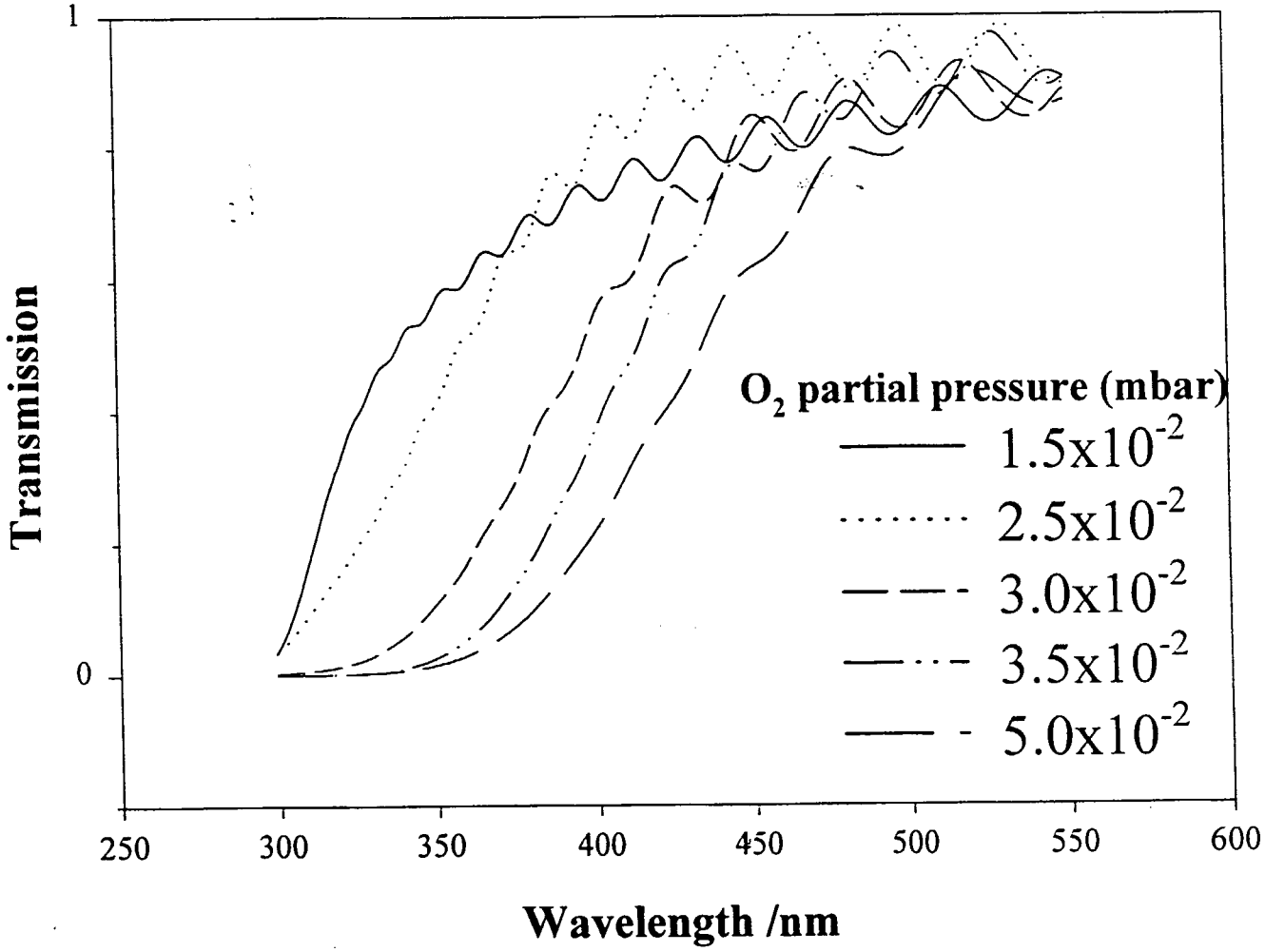
1
0
Transmission
250
300
350
400
450
500
550
600
Wavelength /nm
O2 partial pressure (mbar)
1.5x10-2
2.5x10-2
3.0x10-2
3.5x10-2
5.0x10-2

Fig 2(a)

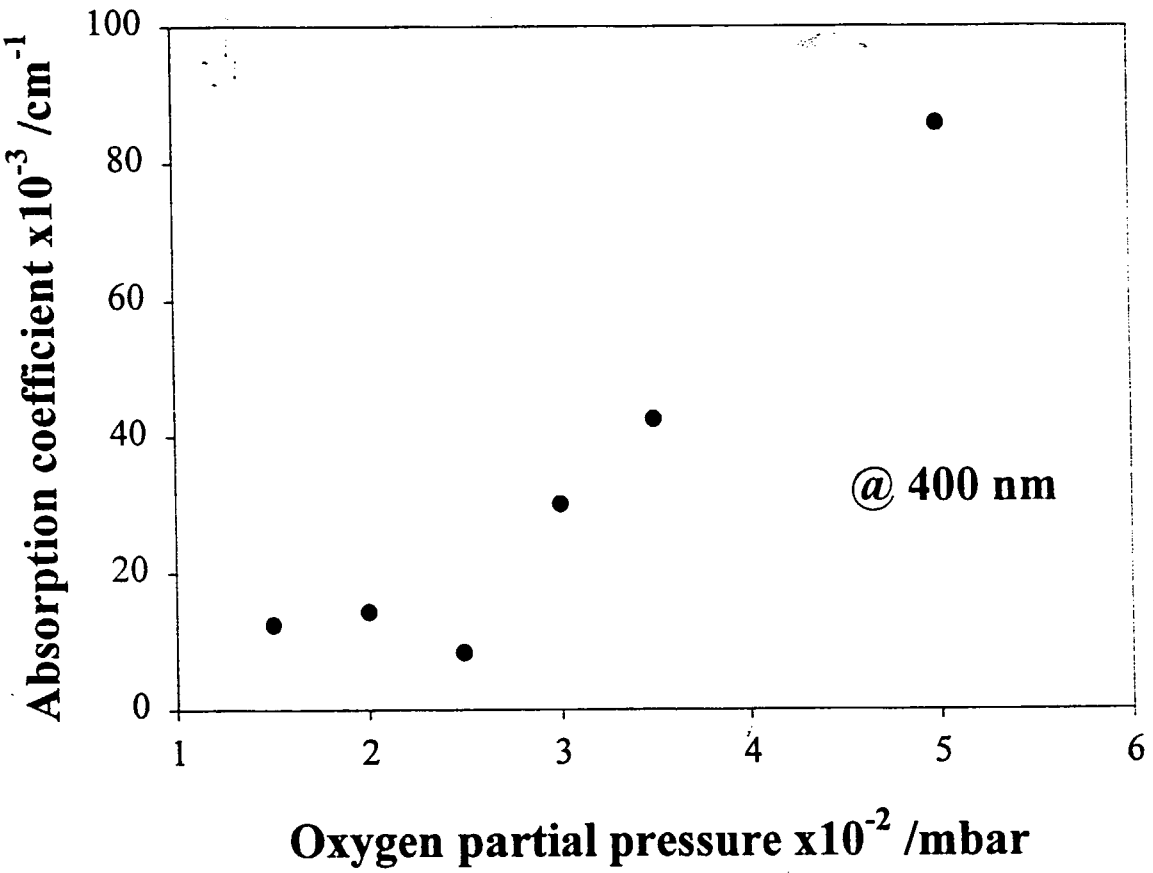
Absorption coefficient x10$^{-3}$ /cm$^{-1}$
100
80
60
40
20
0
1
2
3
4
5
6
@ 400 nm
Oxygen partial pressure x10$^{-2}$ /mbar

Fig 2(b)

Fig 3(a)

Fig 3(b)

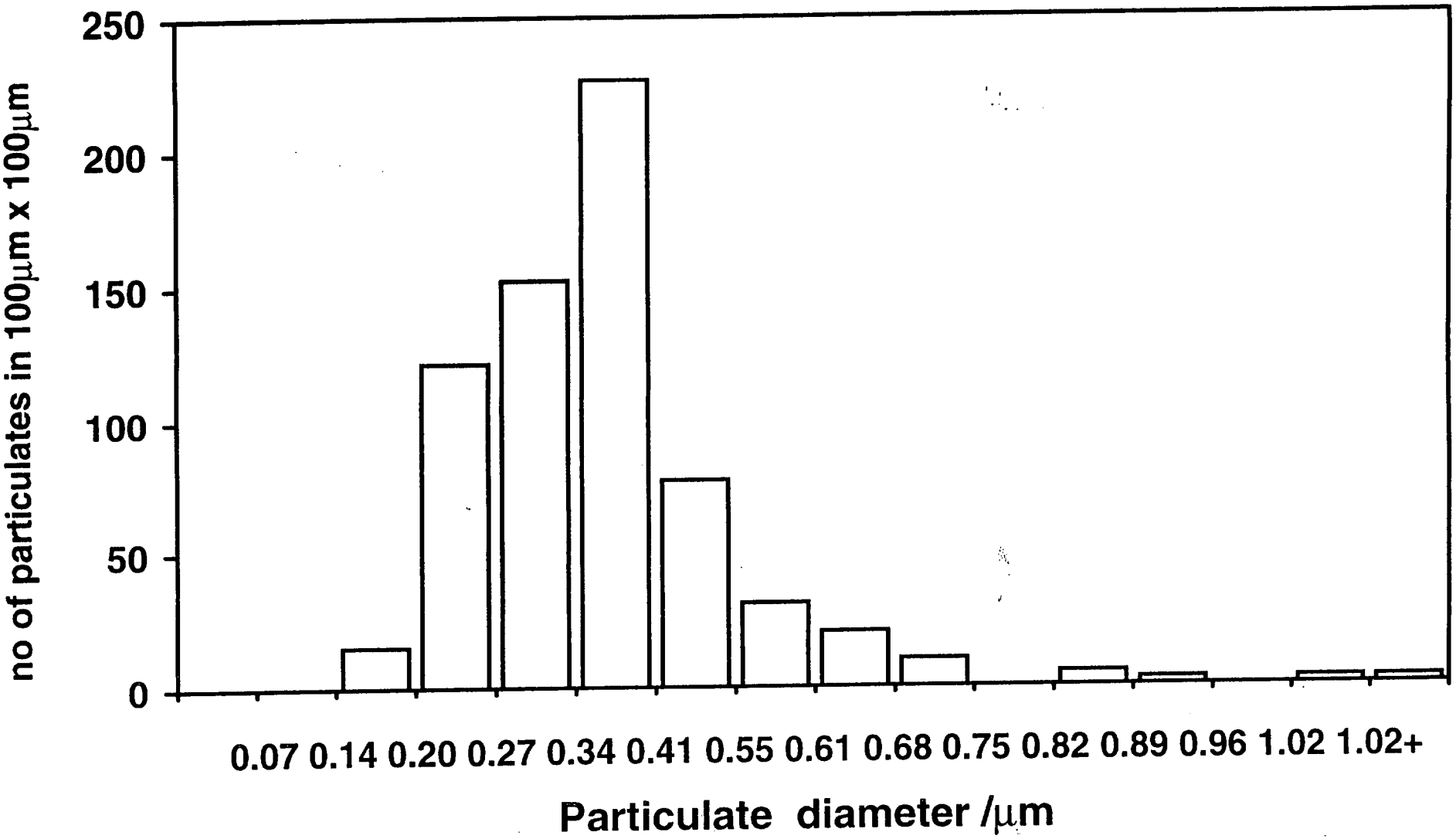
250
200
150
100
50
0
no of particulates in 100μm x 100μm
0.07 0.14 0.20 0.27 0.34 0.41 0.55 0.61 0.68 0.75 0.82 0.89 0.96 1.02 1.02+
Particulate diameter /μm

Fig 4

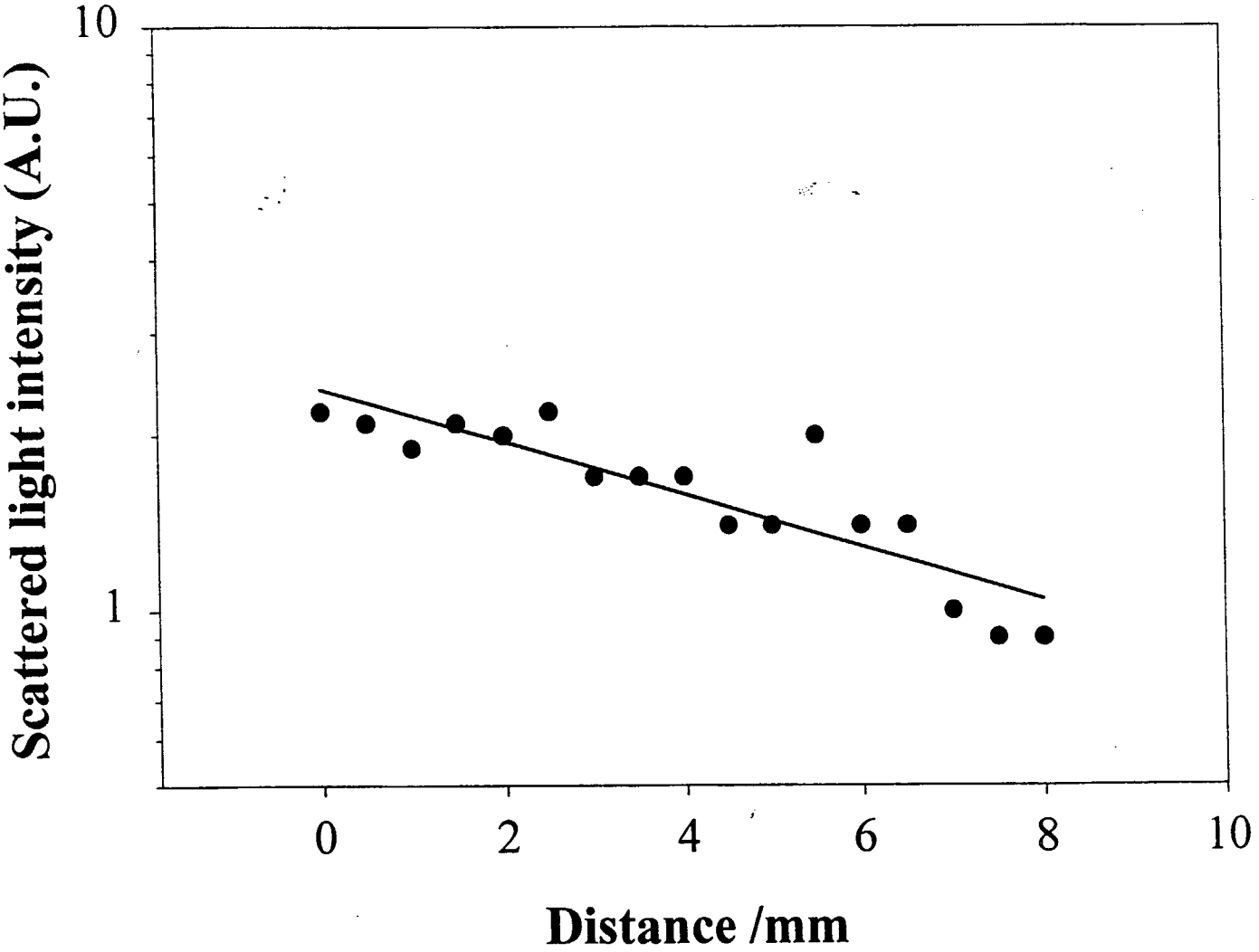


Fig 5.

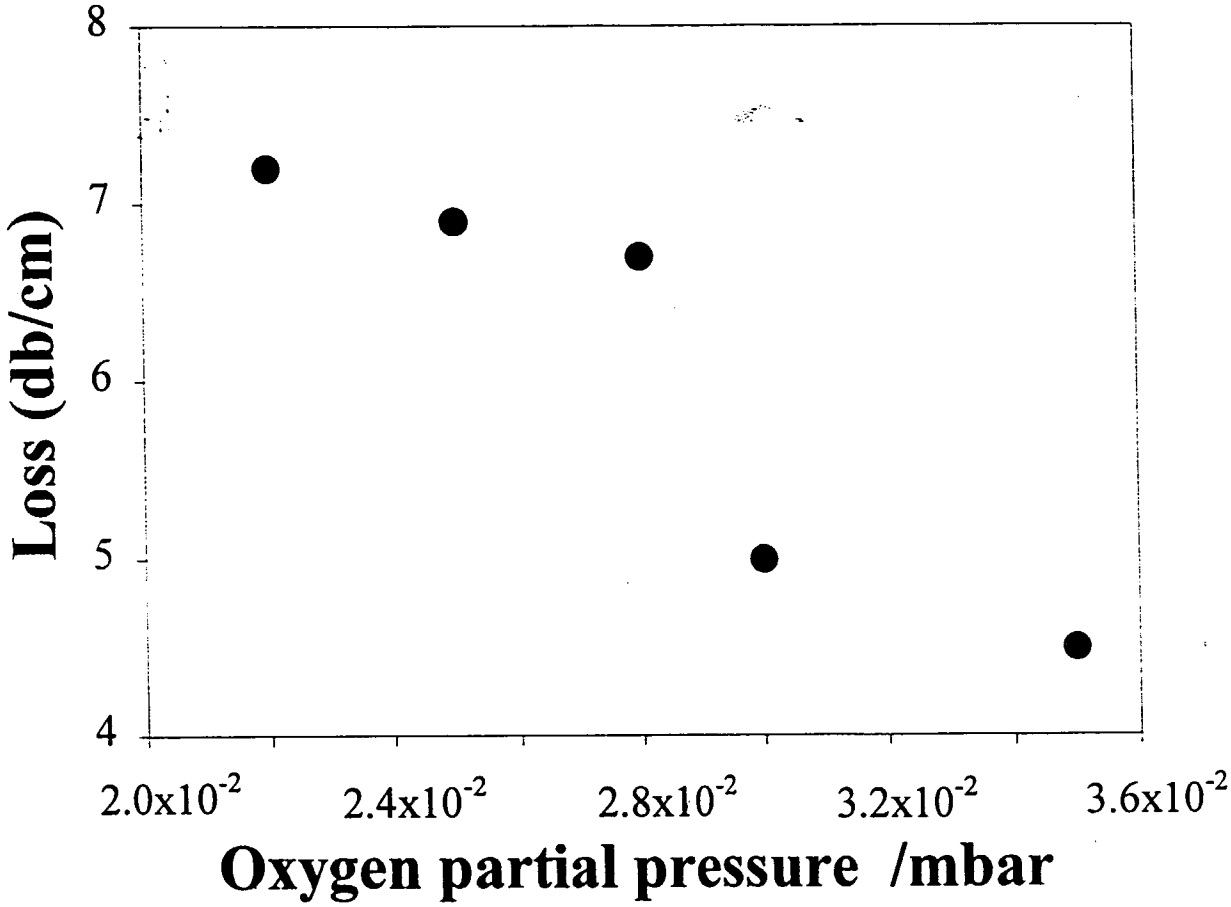
8
7
6
5
4
Loss (db/cm)
2.0x10-2
2.4x10-2
2.8x10-2
3.2x10-2
3.6x10-2
Oxygen partial pressure /mbar

Fig 6.

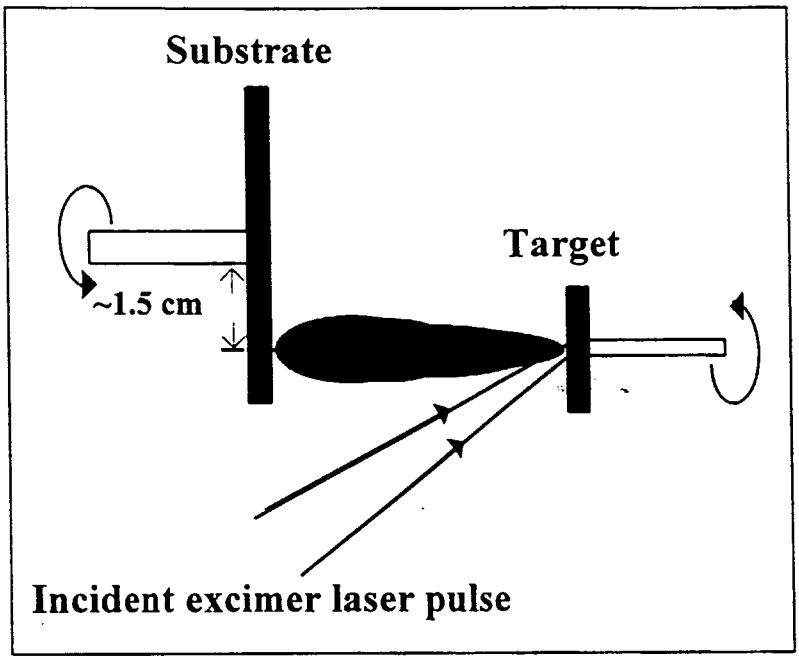


Fig 7.

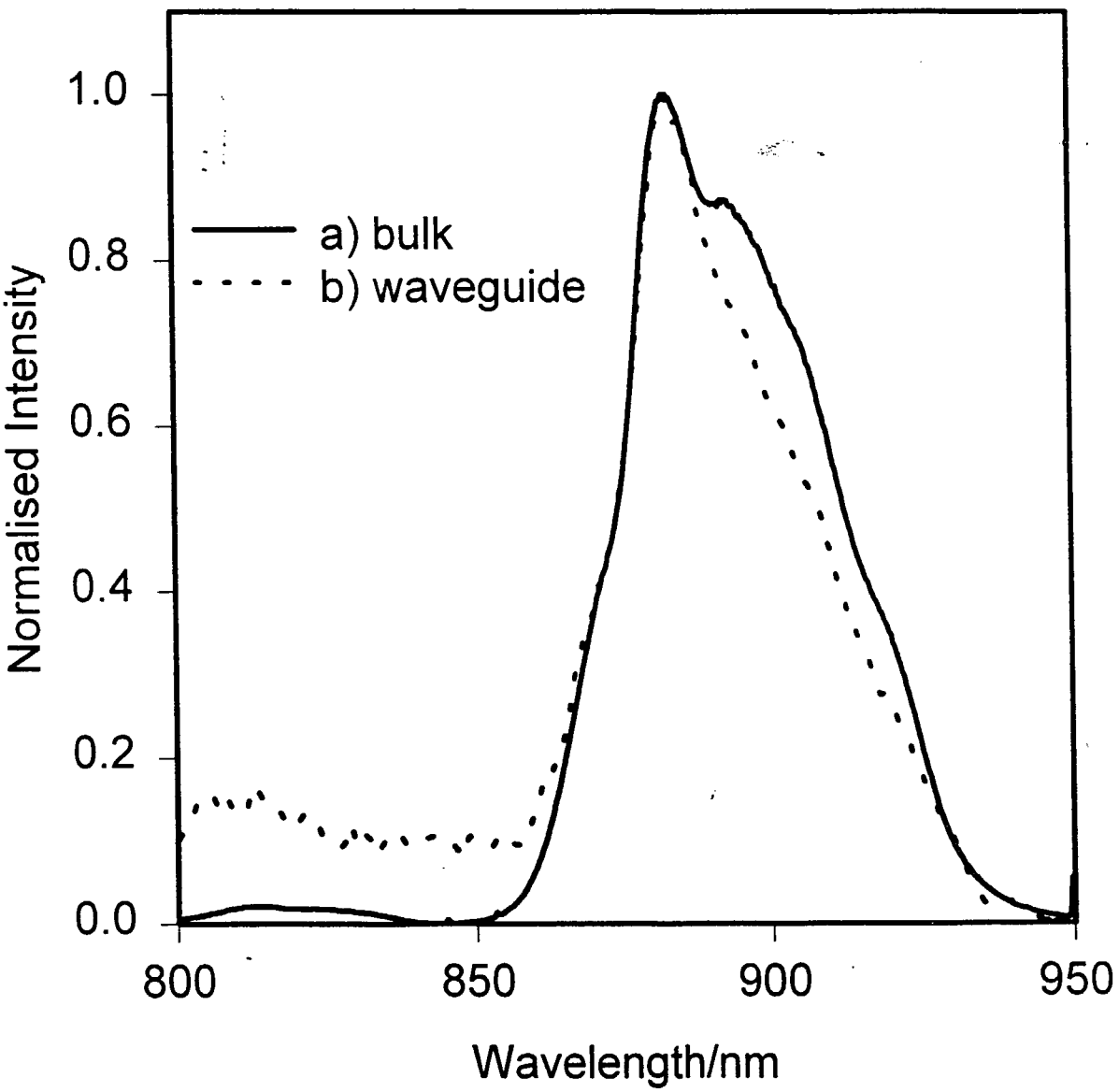
1.0
0.8
0.6
0.4
0.2
0.0
Normalised Intensity
a) bulk
b) waveguide
800
850
900
950
Wavelength/nm

Fig 8